HIGH SOLIDS INTERNALLY U.V. STABILIZED MELAMINE CURED URETHANE PAINT

BACKGROUND OF THE INVENTION

This invention relates to an ultraviolet (U.V.) stable, sprayable, high solids urethane paint composition characterized by a durable, high gloss surface when applied to and cured over a suitable substrate. The invention also relates to a method of making such paint by reacting hindered piperidinol ultraviolet stabilizing agents into a paint resin which is crosslinked by an acid catalyzed, melamine formaldehyde, crosslinking agent at relatively low temperatures.

Urethane coating compositions are well known for their toughness, flexibility, impact resistance, and first class glossy surface finish. However, urethane paints are susceptible to loss of gloss when exposed to ultraviolet radiation (sunlight, e.g.,) and moisture. Thus, they have not generally been considered suitable for use as automotive topcoats.

William T. Short, an inventor of the subject invention, earlier described a U.V. and moisture resistant urethane paint system in U.S. Pat. No. 4,243,792 assigned to the assignee hereof. The patent relates to the incorporation of hindered piperidinol esters of aliphatic carboxylic acids in urethane polymers for U.V. stabilization. The paints were formed by reacting a stoichiometric excess of suitable aliphatic polyisocyanate with a mixture of organic triols, diols and the hindered piperidine stabilizer. The reactions were catalyzed by an organometallic catalyst such as dibutyl tin dilaurate. The paint itself was moisture cured at the unreacted isocyanate groups under conditions of high relative humidity and low temperatures. A disadvantage of this earlier paint system was the presence of the free isocyanate end groups on the uncured paint. These groups are highly reactive necessitating careful handling of the paint to prevent premature reaction, and some people may develop allergic sensitivity upon extended exposure. Thus, it would be preferable to have a paint composition with no appreciable amount of reactive isocyanate groups.

Due to the high volume nature of most automotive paint operations, it is also extremely desirable to increase the resin to solvent ratio. Currently most automotive paint systems are based on sprayed acrylic enamels. In order to obtain the physical and appearance properties required for automotive topcoats, a minimum resin molecular weight of about 15,000 is necessary. However, in this molecular weight range, acrylic resins can generally comprise no greater than about 50 (and usually less than 30) weight percent of the paint. Considerable energy is expended in evaporating solvent from low solids paints in the paint ovens. Moreover, means must be provided for handling fugitive solvent.

Accordingly, it is an object of this invention to provide a sprayable, high solids urethane paint composition that is characterized by a durable high gloss surface finish resistant to ultraviolet degradation. It is a further object of our invention to provide polyurethane paint resin without free isocyanate groups in which a piperidine U.V. stabilizer is chemically incorporated. A more particular object is to incorporate such piperidine U.V. stabilizer in a paint resin which is cured by crosslinking functional hydroxyl groups with an acid catalyzed, melamine formaldehyde crosslinking agent.

Another object of the invention is to provide a method of making such U.V. stable, low energy curing, urethane paint resins by reacting a hindered piperidinol ultraviolet stabilizing agent with excess polyisocyanate and thereafter reacting the product of this reaction with a stoichiometric excess of polyether polyol to create a paint resin that can be crosslinked by means of an acid catalyzed melamine formaldehyde crosslinking agent.

A specific object of the invention is to provide a production sprayable, low viscosity automotive quality topcoat paint formulation containing a minimal amount of volatile solvent. Another specific object is to create such a high solids paint which will cure in a relatively short period of time at relatively low temperatures.

BRIEF SUMMARY OF THE INVENTION

In accordance with the preferred practice of our invention, these and other objects may be accomplished as follows. An acid catalyzed, melamine formaldehyde crosslinkable polymer binder resin is prepared by mixing a hindered piperidine having a functional hydroxy group (herein piperidinol) ultraviolet stabilizing agent with a substantial stoichiometric excess of a polyfunctional isocyanate. The reaction yields a piperidine group-terminated isocyanate prepolymer. A preferred piperidinol U.V. stabilizer is 2,2,6,6-tetramethyl-4-piperidinol (TMP-4-OH), and a preferred aliphatic isocyanate is methylene bis(4-cyclohexyl isocyanate) (H_{12}MDI). The isocyanate terminated prepolymer is then reacted with a stoichiometric excess of polyether polyol, preferably a mixture of polyoxypropylene diols and triols. The ratio of diols to higher functionality polyols may be adjusted to provide desired hardness, toughness and flexibility in the cured paint. In a preferred formulation, approximately equal chemically equivalent amounts of diol, triol and diisocyanate (i.e., about one third of the total equivalents each) are present in the paint resin compositions along with a few percent piperidinol U.V. stabilizer on an equivalent basis.

The initial reaction of the piperidinol and excess isocyanate creates an isocyanate terminated constituent having piperidine U.V. stabilizer attached to an end of a portion of the diisocyanate molecules. The piperidine attachment is a urethane linkage formed at the functional hydroxyl group of the piperidinol starting material. This urethane bond is stable during the subsequent reaction of the diisocyanate prepolymer with the polyols and during the acid crosslinking of the resin. That is, the crosslinking brought about by the reaction of a melamine formaldehyde in the presence of a weak acid catalyst does not displace the piperidine in the paint resin. It is therefore reacted into the cured paint to stabilize it against U.V. degradation. A competing reaction between the isocyanate and the piperidinol is the formation of weak urea linkage between the nitrogen of the piperidine ring and the isocyanate end groups. However, this linkage did not appear to be stable with respect to subsequent reaction with either the polyol or the acid catalyst used for crosslinking.

The preferred crosslinking agents for the subject paint resins are partially methylated melamine resins. These are made by prereacting less than 6 moles of formaldehyde (preferably about 3 moles) with each mole of melamine. The reaction causes the addition of hydroxymethyl groups to the amine groups of the melamine resin. In acid environments (pH preferably less than 5) at elevated temperatures (preferably about 250° F.), these melamine formaldehydes react with the hy-